A STUDY OF THE EFFECT OF VARIOUS ANIONS ON THE EXCHANGE REACTION BETWEEN ZINC METAL AND ZINC ION

An abstract of a Thesis by
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This study was undertaken to determine what effect if any the concentration of various anions have on the exchange reaction between zinc metal and zinc ions. A search of the literature was done to gain information on the existence of zinc chloride complexes since the formation of these complexes was postulated to be an important factor in any effects on the exchange that might be observed. It was found that the predominant complex appears to be $[ZnCl_4(H_2O)_2]^{2-}$.

The study of the effects of anions on the zinc metal zinc ion exchange was done in two parts. In the first part the effects of 1 M solutions of $ZnCl_2$, NaCl, NaBr, $NaClO_4$, and $NaNO_3$ were studied using Zn^{65} as a tracer in the exchange reaction. It appeared that NaCl enhanced the rate, NaBr had little effect on the rate, and $ZnCl_2$, $NaClO_4$, and $NaNO_3$ retarded the rate of exchange.

In the second part the effect of various concentrations of chloride were studied again using Zn^{65} as a tracer. It was found that maximum exchange occurs at a concentration around 0.1 M NaCl.

A STUDY OF THE EFFECT OF VARIOUS ANIONS ON THE EXCHANGE REACTION BETWEEN ZINC METAL AND ZINC ION

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INTRODUCTION

There are many instances when two seemingly unrelated chemical reactions are found, on closer examination, to go by similar reaction mechanisms. One way of determining whether two reactions progress through the same mechanism is to study effects of different conditions on the progress of the reactions.

A study was conducted for the reaction of zinc metal with hydrochloric acid by Rider (20). In this study he determined the effect of the concentration of various anions on the rate of hydrogen evolution. It was shown that halide ions enhance the rate of reaction, that perchlorate and sulfate ions retard the rate of reaction, and that nitrate ion renders the zinc metal passive. Rider also showed that excess zinc ion retards the rate of the reaction.

A reaction which may go by a mechanism similar to the zinc and hydrochloric acid reaction is the exchange reaction between zinc metal and zinc ions. As can be seen from Equations I_a and I_b, both reactions involve transfer of electrons from a zinc atom to an electron deficient ion.

$$\text{Eq. } I_a \qquad Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$$

$$\text{Eq. } I_b \qquad Zn + Zn^{*2+} \longrightarrow Zn^{*} + Zn^{2+}$$

If it can be shown that various anions have effects on the

rate of exchange of zinc with zinc ion that are similar to the effects that these anions have on the rate of oxidation of zinc by hydrochloric acid then it is possible the two reactions have similar mechanisms.

The purpose of this study is to determine the effects of various anions on the exchange reaction between zinc metal and zinc ion and to compare these effects to those of the anions on the zinc and hydrochloric acid reaction.

REVIEW OF LITERATURE

There have been many data collected that indicate that there are several factors affecting the rate of solution of zinc in acids. One factor as shown by Bouchet (2) is the purity of the metal. He showed that 99.9999% pure zinc reacts slower in hydrochloric acid and sulfuric acid than do less pure samples.

Another factor affecting the reaction rate of the zinc acid system is the form of the zinc. According to Luce (17) there is a relationship between the curvature of the surface of zinc metal and the rate of solution in acids. Dvorkin and Durdin (9) did some work that showed that cast zinc dissolves more readily than rolled zinc.

Much work has been done to determine the mechanism of the solution of zinc in acid. Roehl, King and Kipness (23) concluded that the rate of solution of zinc in HCl is controlled by diffusion of acid through a layer in which a concentration gradient has been set up. Later work by Welsh and Garret (27) with zinc and hydrochloric acid in methanol substantiates the conclusion of Roehl, King, and Kipness. Leipina and Tetere (16) postulated that the reaction of zinc involves first the formation of a zinc hydride on the surface and second, the reaction of hydride with hydrogen ion to give hydrogen gas and zinc ion.

A number of investigators have found that various

factors promote or inhibit the zinc and acid reaction. It has been found that isocyanates (3), thiocyanates (22), chloride (22), bromide (22), iodide (22), and the salts of iron (18), lead (18), arsenic (18), bismuth (18), cobalt (18), copper (18), silver (18), nickel (18), and antimony (18) accelerate the reaction. Substances that have been found to inhibit the reaction are: Hydrogen peroxide (20), potassium bromate (20), sodium dichromate (15), citric acid (15), hydrocyanic acid (13), nicotinic acid (10) nitrate ion (22), and phosphate ion (22). Dvorkin and Durdin (9) found that the rate of solution of zinc in acid increases exponentially with acid concentration.

The solution of zinc in various systems has been studied. Balakrishnan and Venkatensav (1) studied the effect of various solutions on the range of potentials observed in dissolving zinc from brass. They found that in solutions containing SO_4^{-2} the range of potentials observed was wider than the range observed in solutions containing Cl^-. A study of the effect of metal oxides on the dissolution of zinc in aqueous sodium methylsiliconate was done by Rudzite, Lagzdins, Sakne, and Kukurs (24). They found that the rate of evolution of hydrogen varied from maximum to minimum with various oxides in the order $FeO > Co_2O_3 > V_3O_5 > CuO$.

Various systems have been found to be affected by addition of sodium chloride. James (14) found that sodium chloride had little effect on the rate of solution of

magnesium in undissociated acids but, sodium chloride increased the rate of solution of magnesium in highly ionized acids. In work done by Zimmerman and McDonald (28), it was shown that sodium chloride increased the rate of solution of cadmium in hydrochloric acid. This change in rate was explained by postulating that cadmium ion was being complexed by excess chloride ion.

A number of studies have been conducted involving the exchange of zinc ions with other species. The exchange of zinc ions with zinc electrode was investigated by Dirkse and Hampson (8). They found that the ionic strength affects the exchange. Piro, Bernhard, Branica and Verzi (19) found that in a solution which has 34 ppt sodium chloride with a complexing agent, Zn^{65} is completely exchanged in both complexed and noncomplexed species in one hour. In sea water the exchange occurred only in the ionic and particulate fractions. After one year no exchange occurred in the complexed fraction. In an investigation by Quintin and Collier (21) it was found that the rate of exchange between a zinc amalgam and a zinc salt solution was affected by chloride ion but was not affected by perchlorate ion.

Much evidence has been found to support the formation of chlorozincate complexes. Hixon (11) found that when zinc and barium were dissolved in hydrochloric acid and the solutions then subjected to a potantial difference,

mid-range concentrations showed a migration of zinc containing ions to the anode while dilute and more concentrated solutions showed a migration of zinc containing ions to the cathode. This observation suggests that negative complex ions are being formed at the medium concentrations. Work done by Desai (6) using interfacial tension curves of mixed solutions of chloride and zinc showed that zinc chloride forms various halozincate complexes, depending upon the concentration of substances present. Using Raman spectroscopy Delwaulle (5) showed that in zinc chloride solutions the spectra obtained coincide with that of $[SnBr_4]$ indicating the presence of $[ZnX_4]^{2-}$. Titov (25) studied volume changes for the sodium chloride-zinc chloride system by varying the concentration of zinc chloride from 0 - 100% in sodium chloride. He found volume changes corresponding to the formation of chlorozinc complexes with $Na_2[ZnCl_4]$ being the most stable. Dessy and Coe (7) found evidence for the possible formation of RZnX.

Some interesting information regarding the halide complexes of zinc was found in a text by Cotton and Wilkinson (4). The data in Table I and Table II were taken from this text. These data show that zinc complexes are less stable than cadmium or mercury complexes. It was also stated that the effects of ionic strength on complex formation are rather large.

Table I. Equilibrium constants for some typical complexes of Zn, Cd and Hg.
($M^{2+} + 4X = [MX_4]$; $K = [MX_4]/[M^{2+}][X]^4$)[a]

X	K		
	Zn^{2+}	Cd^{2+}	Hg^{2+}
Cl^-	1	10^3	10^{16}
Br^-	10^{-1}	10^4	10^{22}
I^-	10^{-2}	10^6	10^{30}
NH_3	10^9	10^7	10^{19}
CN^-	10^{21}	10^{19}	10^{41}

[a]This entire table was taken from Cotton and Wilkinson (4).

Table II. Some formation constants of zinc and cadmium halide complexes (at 25°)[a]

Halogen		Log K_1	Log K_2	Log K_3	Log K_4	Medium
Zn	F	0.75	Not obs.	Not obs.	Not obs.	0.5-1.0 M $NaClO_4$
	Cl	-1.0 to +1.0	-1.0 to +1.0	-1.0 to +1.0	-1.0 to +1.0	Variable
	Br	-0.60	-0.37	-0.73	0.44	Ionic str. = 4.5
	I	-2.93	1.25	-0.07	-0.59	Ionic str. = 4.5
Cd	F	0.46	0.07	Not obs.	Not obs.	1.0 M $NaClO_4$
	Cl	1.77	1.45	-0.25	-0.05	2.1 M KNO_3
	Br	1.97	1.25	0.24	0.15	1 M KNO_3
	I	2.96	1.33	1.07	1.00	1.6 M KNO_3

[a]This entire table was taken from Cotton and Wilkinson (4).

MATERIALS AND METHODS

It was proposed to determine the effect of the concentration of various ions on the zinc metal/zinc ion exchange reaction and to explain the effects observed. At the start of the investigation it was postulated that any effects observed would probably be due to the formation of zinc complexes. Three main experiments were carried out as part of this investigation.

Part I. Investigation of Zinc Chloride Complexes

In the first step an attempt was made to verify the formation of zinc complexes and to identify the more predominant species formed. This verification was attempted by the method of Vosburgh and Cooper (26) of continuous variations. Ultraviolet spectra were obtained with a Beckman DK-2A recording spectrophotometer. The procedure consisted of preparing solutions containing various ratios of zinc to chloride using 0.10 M zinc sulfate and 0.10 M sodium chloride and keeping the sum of zinc ion concentration and chloride ion concentration equal to 0.10 M. Each solution was made by combining a predetermined volume of 0.10 M zinc sulfate with enough sodium chloride to make ten milliliters of solution. For example, eight milliliters of 0.10 M zinc sulfate were combined with two milliliters of sodium chloride to produce a sample which was 0.08 M in zinc

sulfate and 0.02 M in sodium chloride. The solutions were placed in silica cuvettes and the percent transmittance was measured for each solution at a wavelength of 192 nm. Zinc sulfate at a concentration of 0.10 M was used as the blank.

The preceding procedure was repeated substituting hydrochloric acid for sodium chloride and using sulfuric acid to keep the pH at a value 1.0. The percent transmittance of these solutions, in silica cuvettes, was measured at 192 nm. Since erratic values were obtained a scan of all the wavelengths from 360 nm to 180 nm was made measuring percent transmittance for all of the solutions used in the earlier trials. This experiment was done to determine which zinc ion ratio was most favorable for the formation of complex ions.

Part II. Determination of the Effect of Concentration of Various Ions on the Zinc/Zinc Ion Exchange Reaction

In the second step of the investigation it was proposed to determine the effect of the concentration of various anions and the type of anion present on the exchange reaction between zinc metal and zinc ions in a certain period of time. This determination was made by weighing out 0.5 grams of twenty mesh granulated zinc metal, measuring its activity on a Baird Atomic model 530 gamma ray spectrophotometer and placing it in five milliliters of 1 M solution of a salt containing an anion of ineterest that

was tagged with 100λ of a solution of Zn^{65} in HCl. After placing the zinc metal in the tagged solution the combined metal and solution were placed in a gamma ray spectrophotometer to measure the initial activity present. Upon removal from the spectrophotometer the zinc and solution were allowed to react for two hours. After reacting for two hours the solution was decanted and the zinc metal was washed twice with five milliliters of water and once with five milliliters of acetone. The metal was then dried on a hot plate and placed in the gamma ray spectrophotometer to measure the activity retained by the metal. This activity was compared to the initial activity of the zinc metal and the initial activity of the metal and solution. This procedure was repeated for solutions of various anions. It was also repeated varying the concentration of the anion in the solution.

Part III. Determination of the Effect of Concentration of Anions on the Rate of Zinc/Zinc Ion Exchange Reaction at Constant Ionic Strength

The third and final step of the investigation was conducted in much the same way as the second step. In this third step it was proposed to determine the effect of the concentration of various anions on the rate of the zinc/zinc ion exchange reaction. Half gram samples of twenty mesh granulated zinc were weighed out and the activity measured on the gamma ray spectrophotometer. The zinc samples were

then exposed to five milliliters of solution tagged with Zn^{65}. The exposure times were one half hour and two hours. At the start of this time the combined metal and solution was placed in the spectrophotometer and the initial activity was measured. At the end of the exposure time the solution was decanted and the metal was washed twice with water and once with acetone and dried on a hot plate. The metal was then placed in the spectrophotometer and the activity was measured. The activity retained by the metal was calculated by subtracting the activity of the unreacted zinc from the activity of the reacted zinc.

The data obtained by the preceding methods, and the mathematical and graphical treatment of these data are shown in the following section.

RESULTS AND DISCUSSION

Part I. Investigation of Zinc Chloride Complexes

At the start of the investigation it was postulated that any effects observed would probably be due to the formation of zinc complexes. Since the main species of interest was the chloride ion it was decided to attempt to determine which if any chlorozinc complexes form. The method that was used in this determination was the spectrophotometric method developed by Vosburgh and Cooper (25) to determine the number of ligands around the central atom of a complex. After numerous unsuccessful attempts it was decided that no reliable data could be obtained with the available equipment due to the fact that the wavelengths of interest were too near the limits of the instrument being used.

Since it was important to establish the existence of chlorozinc complexes and the identification of the most prominent ones and in light of the fact that this could not be done experimentally with the available equipment it was decided to search the literature for the needed information. The search was conducted to find either an experimental procedure that could be used or a report of an investigation that had established the identification of the chlorozinc complexes. The latter was found.

A report of a Raman study of zinc chloride solutions by Irish, McCarroll, and Young (12) was found. The study was conducted to obtain a detailed knowledge of the chemical species in zinc chloride solutions. Both photographic and photoelectric detection were used. A 7.61 M solution of zinc chloride was used as a standard reference. Three types of solutions were studied: (a) zinc chloride at concentrations of 2.19 M, 7.61 M, and 13.0 M, (b) zinc chloride at concentrations of 2.14 M and 1.41 M with excess chloride added in the form of lithium chloride, ammonium chloride, or hydrochloric acid, and (c) zinc chloride in butanol at a concentration of 0.58 M. The Raman band assignments that were made and the species thought to be present are shown in Table III. The band assignments were made from intensity studies. For example, the band at 278 cm^{-1} was assigned to $[ZnCl_4(H_2O)_2]^{2-}$ because it was noted that the intensity of this band increased as a stoichiometric ratio of four chloride ions to one zinc ion was approached.

The Job method was used to establish the number of chloride ions associated with each zinc ion in the most predominant complex. Keeping the total zinc plus chloride concentration of 11 M while varying the zinc to chloride concentration ratios the intensities of the 278 cm^{-1} band were measured. These intensities were plotted against f which is the ratio of the total concentration of chloride

Table III. Raman frequency for various species found in zinc chloride solutions.[a]

Frequency (cm^{-1})	Species	Concentration range
390 ± 10	$[Zn(H_2O)_6]^{2+}$	<13 M
110 278	$[ZnCl_4(H_2O)_2]^{2-}$	<10 M
305	$[ZnCl_2]$	> 4 M
>305	$[ZnCl]^{+}$	< 4 M

[a]This table was condensed from Table II in the article by Irish, McCarroll, and Young (12).

ion to the sum of the total concentration of zinc ion and chloride ion. This plot is shown in Figure 1. At the maximum obtained in Figure 1 f is related to the number of ligands around a zinc ion by the formula $n = f/1 - f$. A value of 4.1 ± 0.3 was obtained for n.

Evidence for the presence of $[ZnCl]^{+}$ was found in solutions that were less than 4 M in zinc chloride. The existence of $[Zn(H_2O)_6]^{+2}$ was indicated only in solutions that did not contain an excess of chloride ion. No evidence for the existence of $[ZnCl_3]^{-}$ was observed.

Part II. Determination of the Effect of Concentration of Various Ions on the Zinc/Zinc Ion Exchange Reaction

In the second step of the investigation it was decided to determine what effects, if any, various complexing and non-complexing species would have on the exchange reaction between zinc metal and zinc ion at a particular time after initiating the reaction. The amount of exchange between zinc and zinc ion enriched with radioactive Zn^{65} was measured. First the activity of untreated zinc metal was measured by placing 0.5 grams of twenty mesh zinc metal in a 25 milliliter erlenmeyer flask and placing the flask in the sample well for the counter. The activity of untreated zinc metal was measured four different times and was found to be equal to the background activity measured with nothing in the sample well of the counter. Next, the

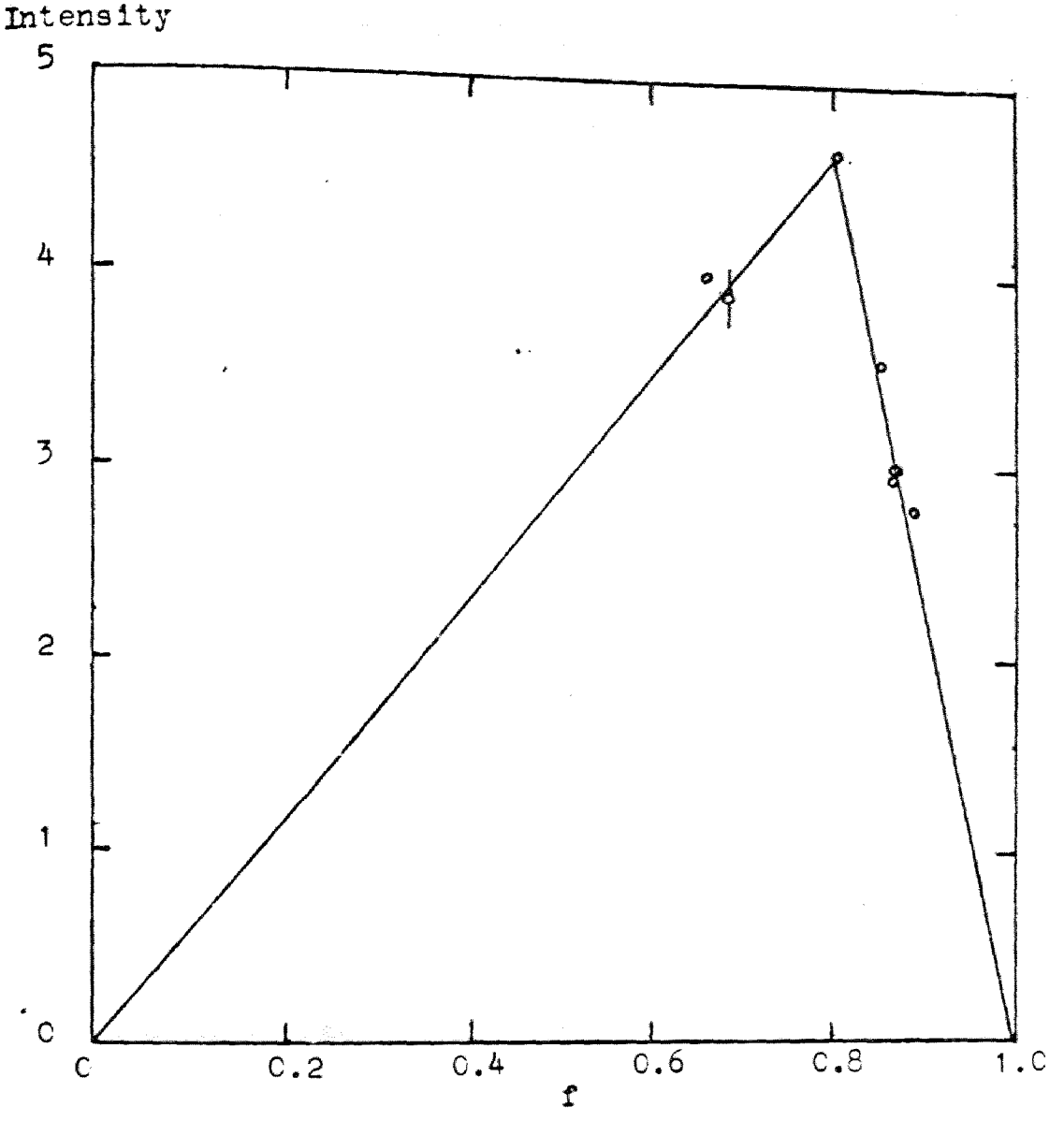

Figure 1. Intensity of the 278 cm^{-1} line versus the ratio, f, of the total concentration of chloride ion to the sum of the total concentrations of chloride and zinc. (Taken from FIG.4 Irish, McCarroll, and Young (12)).

determination of a suitable period of time to allow the reaction to proceed was made. This period was determined by exposing 0.5 grams of zinc to five milliliters of water containing 100λ of radioactive zinc as Zn^{65}. The exposure times were varied from one half hour to twenty-four hours. The data obtained are summarized in Table IV.

Table IV. The average activity absorbed by 0.5 grams of 20 mesh zinc metal from five milliliters of water containing Zn^{65} with an initial activity of 11,300 counts per minute.

Time	0.5hr	2hr	3hr	24hr
Average counts per minute	440 ± 20[a]	820 ± 30	830 ± 25	4700 ± 18

[a]These are standard deviations.

It was decided that two hours was a sufficient amount of time to allow for significant exchange between the zinc metal and Zn^{65} ions. From the data it can be seen that the exchange rate slows after two hours. Since all that was necessary was to get a significant exchange, it was not necessary to allow the exchange to take any longer.

After the proper time period was determined solutions of various anions were tagged with Zn^{65} and placed in flasks containing zinc metal to see what the effect would be on the exchange of the Zn^{65} ion with zinc metal. Sodium chloride and sodium bromide were used as complexing

agents since it was known that chloride ion would form complexes and it would seem that bromide should act similarly. Sodium perchlorate was used as a noncomplexing agent because it is well documented in the literature that perchlorates do not form complexes (4). Sodium nitrate was used because Rider (22) found that nitrates made zinc metal passive to hydrochloric acid and it was decided to see if similar effects were observed in the zinc exchange reaction.

Zinc chloride itself was not used since preliminary experiments showed that very little exchange was observed in this solution. This phenomenon would seem to be related to the observation made by Rider (22) that excess zinc ion retards the reaction of zinc with HCl. However, I feel that the causes are different. The phenomenon observed by Rider is probably due to a shift of the equilibrium of the reaction shown in Equation II.

Eq. II $$Zn + 2H^{+} + 2Cl^{-} \rightleftharpoons Zn^{+2} + H_2 + 2Cl^{-}$$

If the concentration of Zn^{+2} is increased the equilibrium would shift to the left and the evolution of H_2 would be reduced. The phenomenon observed in the present experiment is probably best explained by the fact that in five milliliters of 1 M zinc chloride tagged with 100λ of 0.1 M Zn^{65} ion there would be five hundred more untagged zinc ions than tagged zinc ions. Therefore, the likelihood of exchange with an untagged ion is much greater than it is with

a tagged ion. As a result little exchange with Zn^{65} ions is observed.

As a standard procedure the exchange was carried out in five milliliters of water. Solutions of 1.0 M concentration were prepared for each of the compounds used. Five milliliters of each solution were placed in separate 25 milliliter erlenmeyer flasks along with 0.5 grams of twenty mesh zinc metal. The samples were spiked with 100λ of Zn^{65} solution. Each flask containing a tagged solution was placed in the sample holder of the counter and counted. Each sample was counted three times for one minute. The three counts were then averaged to obtain the count for a single trial. This was called the initial count (I). After two hours ± 5 min the solution was decanted and the metal was washed twice with water and once with acetone before drying on a hot plate. Each flask containing the dry zinc metal was placed in the sample well of the counter and counted for one minute. Each sample was counted three times. The three counts were averaged and the average value was used as the count for each trial. This was called the retained count (R). The data obtained from the solutions are summarized in Table V.

The scatter in the counting data is due to the differences in activity in the original Zn^{65} solutions obtained from suppliers and the large amount of scatter in these data was due to the fact that most of the counts were

Table V. Ratio of the activity (R) from Zn^{65} absorbed by 0.5 grams of 20 mesh zinc metal in five milliliters of solution (S) containing 100λ of a solution containing Zn^{65} ion to the initial activity (I) in the solution (S).

Solution	Initial count (I)[a]	Counts retained (R)[a]	R/I[a]	Mean R/I
1 M $ZnCl_2$	2872	0	0.000	0.012±0.015[b]
	4345	13	0.003	
	1354	51	0.038	
	1146	7	0.006	
1 M $NaClO_4$	3346	1236	0.369	0.40±0.15
	4246	1389	0.327	
	1571	1002	0.638	
	1348	330	0.245	
1 M NaCl	3328	1785	0.536	0.49±0.15
	4536	1973	0.435	
	1104	768	0.696	
	1051	313	0.298	
1 M NaBr	1211	867	0.716	0.45±0.20
	1103	247	0.224	
	64391	26003	0.404	
1 M $NaNO_3$	1284	588	0.459	0.33±0.13
	1247	243	0.195	
H_2O	1919	907	0.473	0.44±0.07
	762	405	0.531	
	2592	1072	0.414	
	3260	1126	0.345	

[a]The counts shown are averages of three measurements minus the background count measured with nothing in the sample well of the counter.

[b]These are standard deviations.

low which tends to magnify the statistical errors in counting. Even so, from the data it can be seen that the maximum exchange for the two hours was seen in the solution containing 1 M sodium chloride. Comparing the exchange in sodium chloride to the exchange in water it appears that the sodium chloride increases the exchange slightly. However, sodium bromide appears to have little, if any, effect on the exchange. The noncomplexing sodium perchlorate appears to retard the exchange when compared to water and sodium nitrate appears to retard the reaction even further. No conclusion could be reached regarding the exchange in zinc chloride because the amount of activity measured was so small and inconsistent that it was inconclusive.

After establishing that chloride did appear to increase the exchange taking place it was decided to investigate the effect that varying the concentration would have on the amount of exchange observed. This experiment was done by placing 0.5 gram samples of zinc metal in ten milliliters of sodium chloride solutions that varied in concentration from 1 M to 0.1 M. Again the solutions were spiked with 100λ of the Zn^{65} solution. A sample of zinc metal was also placed in ten milliliters of water containing 100λ of Zn^{65} to use as a reference. Initial and final counts were made as in the preceding experiment. The data obtained from this procedure are summarized in Table VI.

Since these experiments were carried out in twice

Table VI. The ratio R/I where I is the initial activity measured in a sample of 10 ml of solution (S) containing 100λ of Zn^{65} solution and 0.5 grams of 20 mesh zinc metal and where R is the measured amount of activity absorbed by the metal.

Solution	Initial count (I)[a]	Counts retained (R)[a]	R/I[a]	Mean R/I
1 M NaCl	194,764	43,325	0.222	0.224±0.003[b]
	195,272	43,555	0.223	
	193,334	43,653	0.226	
0.5 M NaCl	128,467	36,064	0.292	0.285±0.004
	128,639	36,225	0.282	
	127,682	36,183	0.283	
0.1 M NaCl	70,245	26,646	0.379	0.380±0.003
	70,141	26,431	0.377	
	69,104	26,591	0.384	
0.05 M NaCl	147,038	21,052	0.143	0.144±0.001
	146,748	21,244	0.145	
	145,734	21,055	0.144	
1 M $NaClO_4$	193,723	40,828	0.211	0.211±0.001
	194,036	40,785	0.210	
	193,880	40,841	0.211	
0.5 M $NaClO_4$	239,586	48,483	0.202	0.201±0.001
	238,085	47,913	0.201	
	238,544	47,993	0.201	
0.1 M $NaClO_4$	229,681	38.465	0.167	0.169±0.001
	228,958	38,883	0.170	
	229,028	38,653	0.169	
H_2O	30,201	4,901	0.162	0.165±0.002
	29,109	4,883	0.168	
	29,533	4,895	0.166	

[a]All of the counting data shown are averages of three measurements minus the background measured with nothing in the sample well of the counter.

[b]These are standard deviations.

the volume used in preceding experiments it was expected that the exchange would not be as great in these experiments as it was in the previous experiments because the concentration of Zn^{65} in each solution would only be one half the concentration of Zn^{65} in the solutions of the previous experiments. An unexpected result was the great increase in exchange exhibited in the 0.1 M chloride solution. This experiment was repeated a number of times and each time similar results were obtained. One possible explanation is that the Zn^{65} is being tied up in complexes with the chloride ion. At higher concentrations of chloride ion the Zn^{65} is tied up in complexes more rapidly than at lower concentrations. Therefore less exchange is observed in the 1 M solution than in the 0.5 M solution and the greatest amount of exchange is found in the 0.1 M solution. The decrease in exchange observed in the 0.05 M solution is inconsistent with this line of reasoning. No explanation for this inconsistency is easily drawn from the available data.

Another conclusion that can be reached upon examining the data in Table VI is that exchange tends to increase with increasing ionic strength, which makes the observed increase in exchange with decreasing chloride ion concentration even more dramatic. This conclusion about ionic strength was reached because of the trend seen in the non-complexing perchlorate samples. More exchange occurs in the

1 M sodium perchlorate than in the 0.5 M or the 0.1 M sodium perchlorate.

Part III. Determination of the Effect of Concentration of Anions on the RAte of Zinc/Zinc Ion Exchange Reaction at Constant Ionic Strength

Since the amount of exchange depended on the concentration and the ionic strength of the solution. It was decided to determine how much effect the ionic strength had compared to the chloride ion concentration on the rate of the reaction. This was done by keeping the ionic strength constant while varying the chloride concentration. If comparable amounts of exchange were observed in these experiments as were observed in the previous experiments then the change in ionic strength would have little effect compared to the effect of the concentration of chloride ion.

The experimental procedure consisted of preparing five milliliter solutions made up of varying amounts of 1 M sodium chloride and 1 M sodium perchlorate solutions to give a constant ionic strength. To each solution was added 0.5 grams of zinc metal and 100λ of Zn^{65}. To determine the effect on the rate of exchange samples were allowed to react for one half hour and for two hour periods. The data obtained in this way are summarized in Table VII.

In comparing the data in Table VII to the data in Table VI it can be seen that at about 0.2 M or 0.1 M chloride ion concentration the amount of exchange seems to increase

Table VII. The ratio R/I observed in 5 ml of solutions of sodium perchlorate with varying chloride concentration and constant ionic strength (μ)[a] where (I) is the initial activity observed in the solution from 100λ Zn^{65} solution and (R) is the measured activity absorbed by 0.5 grams of zinc metal placed in the solution for a specific time.

Volume 1 M NaCl	Volume 1 M $NaClO_4$	$[Cl^-]$	R^b	I^b	R/I
		After 0.5 hr			
5 ml	0	1 M	3376	17852	0.189±0.002[c]
2.5 ml	2.5 ml	0.5 M	2095	20510	0.102±0.003
1 ml	4 ml	0.2 M	2027	17781	0.114±0.001
0.5 ml	4.5 ml	0.1 M	1866	17862	0.104±0.004
0	5 ml	0	1528	19283	0.079±0.001
		After 2.0 hr			
5 ml	0	1 M	4405	17790	0.248±0.003[c]
2.5 ml	2.5 ml	0.5 M	3728	18152	0.205±0.005
1 ml	4 ml	0.2 M	4887	20938	0.233±0.002
0.5 ml	4.5 ml	0.1 M	2587	19010	0.136±0.002
0	5 ml	0	1873	17502	0.107±0.001

[a]The ionic strength was calculated to be 1.0 for all solutions.

[b]All of the counting data shown are averages of at least four trials minus the background measured with nothing in the sample well of the counter.

[c]These are standard deviations.

and then fall off. An inconsistency concerning the effect of ionic strength appears when the data in Table VII is compared to the data in Table VI. The value shown in Table VII for R/I after two hours for 1 M sodium perchlorate solution is much lower than the value given in Table VI for the same solution. Table VII also lists lower values than Table VI for R/I after two hours for 0.5 M, 0.2 M, and 0.1 M chloride ion concentrations. These observations indicate that perhaps the exchange increases as the ionic strength decreases which is exactly the opposite of the conclusion reached using only Table VI and examining the R/I values obtained for sodium perchlorate.

Table VII also indicates that a chloride ion concentration between 1.0 M and 0.2 M give rise to a faster rate of exchange than do lesser concentrations or no chloride ion. This is seen by observing that the amount of exchange increases approximately 100% between the 0.5 hour time period and the two hour time period for the chloride ion concentrations of 0.2 M and 0.5 M while the 0.1 M chloride ion and the solution with no chloride show an increase of approximately 30% between the 0.5 hour period and the two hour period.

CONCLUSIONS

The results of this investigation can be summarized as follows:

1. Chloride ion increases the amount of exchange between zinc metal and zinc ions in solution, bromide ion has little effect on the exchange, perchlorate and nitrate ions retard the exchange.

2. The amount of exchange observed depends on the concentration of chloride ion with the maximum occurring at a concentration around 0.2 M or 0.1 M.

3. No conclusion was reached on the effect of ionic strength on the rate of exchange.

These results compare favorably with the results obtained by Rider (20) using the zinc/HCl system. He found that chloride increased the reaction rate, perchlorate retarded the rate, and nitrate stopped the reaction. This comparison suggests that the zinc/zinc ion and zinc/HCl reactions are going by similar mechanisms.

A number of proposals concerning the mechanism can be made from these results. One is that the mechanism for the exchange reaction involves a phase in which the presence of chloride ion causes the zinc atoms to leave the metal surface more rapidly. One explanation for the atoms leaving more rapidly could be that the chloride ions form a layer of negative charge on the surface of the metal which results

in the formation of partial complexes on the surface of the metal. These partial complexes would then leave the surface of the metal more readily than the uncomplexed zinc atoms would, thus increasing the rate of exchange taking place.

The reason that the nitrate slows the reactions rate is probably due to the formation of insoluble oxides on the surface of the zinc metal which then prohibit the contact of the zinc metal with zinc ions.

Some areas for further investigation are suggested by the results of this investigation. One such area would be to conduct studies to determine what the mechanism for the formation of the chlorozincate complexes is. Another thing that could be done is to investigate the effects of many more complexing agents to see if any others would exhibit the same effects as chloride. Also, more experiments should be done to try to determine the effect of ionic strength on the rate of the zinc/zinc ion exchange reaction.

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